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## Specification

### 1. Title of Invention

Paint and its manufacturing method

### 2. Claims

(1) In the paint of which the solid component consists of magnesium fluoride of the particle size  $0.1\ \mu\text{m}$  or less and 1 or more silanes selected from  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyltriethoxysilane,  $\gamma$ -glycidoxypropylmethyldimethoxysilane,  $\gamma$ -glycidoxypropylmethyldiethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and  $\beta$ -(3,4-epoxycyclohexyl)ethyltriethoxysilane, the paint featured in that the aforesaid magnesium fluoride is 30 ~ 50 weight % of the solid component and the aforesaid silane, as calibrated by silica, is 70 ~ 50 weight % of the solid component.

(2) The paint according to the claim 1 featured in that the aforesaid silane is  $\gamma$ -glycidoxypropyltrimethoxysilane, and also 40 ~ 90 weight % of this  $\gamma$ -glycidoxypropyltrimethoxysilane, as calibrated by silica, has been replaced by 1 member or more of tetraethoxysilane, tetramethoxysilane, tetraisopropoxysilane, tetra n-butoxysilane, tetra sec-butoxysilane, and tetra t-butoxysilane.

(3) Manufacturing method of paint featured in that, in the paint of which the solid component consists of magnesium fluoride of the particle size  $0.1\ \mu\text{m}$  or less and  $\gamma$ -glycidoxypropyltrimethoxysilane, and the aforesaid magnesium fluoride is 30 ~ 50 weight % of the solid component and the aforesaid  $\gamma$ -glycidoxypropyltrimethoxysilane, as calibrated by silica, is 70 ~ 50 weight % of the solid component, 40 ~ 90 weight % of  $\gamma$ -glycidoxypropyltrimethoxysilane, as calibrated by silica, is replaced by 1 member or more of tetraethoxysilane, tetramethoxysilane, tetraisopropoxysilane, tetra n-butoxysilane, tetra sec-butoxysilane, and tetra t-butoxysilane.

(4) The paint according to the claim 1 featured in that the aforesaid silane is  $\gamma$ -glycidoxypropyltrimethoxysilane, and also less than 50 weight % of this  $\gamma$ -glycidoxypropyltrimethoxysilane, as calibrated by silica, has been replaced by 1 member or more of methyltrimethoxysilane, methyltriethoxysilane, and methyltriisopropoxysilane.

(5) Manufacturing method of paint featured in that, in the paint of which the solid component consists of magnesium fluoride of the particle size  $0.1\ \mu\text{m}$  or less and  $\gamma$ -glycidoxypropyltrimethoxysilane, and the aforesaid magnesium fluoride is 30 ~ 50 weight % of the solid component and the aforesaid  $\gamma$ -glycidoxypropyltrimethoxysilane, as calibrated by silica, is 70 ~ 50 weight % of the solid component, less than 50 weight % of  $\gamma$ -glycidoxypropyltrimethoxysilane, as calibrated by silica, is replaced by 1 member or more of methyltrimethoxysilane, methyltriethoxysilane, and methyltriisopropoxysilane.

### 3. Detailed Description of the Invention

#### [Area of application in industry]

The present invention relates to the paint for antireflection coating which is suitable for plastic, in particular for transparent plastic film, and its manufacturing method.

#### [Conventional technology]

Conventionally, a single layer coat of magnesium fluoride has been used for antireflection coating appropriately. For the formation of this single layer coat, it is common to carry it out by the methods such as vapor deposition or sputtering, but in order to attain sufficient coat strength, it is necessary to heat-treat at  $250^\circ\text{C}$  or higher, and therefore, there has been a problem that it cannot be adopted for plastic which is not heat resistant.

Incidentally, the present inventors developed a technology by which the antireflection coat can be formed by a coating method by compounding ultrafine particles (particle size  $0.1\ \mu\text{m}$  or less) of magnesium fluoride with binder, etc.. According to this technology, although the heat drying is still required for the coated layer, the paint, of which the heat resistance matches with that of plastic to be painted, can be used by the selection of the binder. Thus, it became possible to form magnesium fluoride antireflection coat on plastic by the coating method.

According to the conventional methods by vapor deposition or sputtering, it was difficult to carry out coating on large objects because of the limitation of the equipment size, and also, the productivity of these methods was poor, and the coating was expensive. All of these problems have been solved by the aforesaid coating method, and thus it has brought about tremendous merits in industry.

#### [Problems to be solved by the invention]

However, according to the aforesaid technology which enables to form antireflection coat by coating the mixture of ultrafine particles (particle size  $0.1\ \mu\text{m}$  or less) of magnesium fluoride and binder, etc., there has been such a problem that, when it is coated on film, unreacted binder, residual solvent, and in addition, additives such as surfactant (for the stability of dispersion, etc.) and leveling agent (the agent to smooth the surface by surface tension), etc. remain on the coat or bleed out whichever the coating method is used, and when the film is rolled up after the coating, these residues on the surface tend to adhere to the film or transfer, causing so-called blocking phenomenon.

The measure against this problem generally is to compound antiblocking agent in the paint, but since this antiblocking agent is high polymer oil, it is not quite compatible and is slow drying, and further, since it is highly viscous, it generates nonuniformity in the coat, and thus it is the cause of troubles. In particular, since transparency and uniformity

of the coat is required in the antireflection coat, addition of the antiblocking agent is not desirable.

Also, it is important to lower the refractive index of the coat as much as possible in the single layer antireflection coat, magnesium fluoride, which is of low refractive index, is used. However, the refractive index of organic substances is high, 1.45 level for the fluorocarbon polymers and 1.5 ~ 1.6 for other organic substances, and this is not desirable for the antireflection. Namely, when the antiblocking agent is compounded in the paint, it does not only raise the refractive index of the coat as a whole, but also it bleeds out to the coat surface and concentrates on the surface so that it raises the refractive index of the surface and thus increases the reflectivity, which is not desirable. In this manner, it is not preferable to add the antiblocking agent to the antireflection coat, and the paint which does not contain the antiblocking agent has been desired.

[Method to solve the problems]

The present inventors carried out intensive studies in the light of the aforesaid situation, and as a result, found that the paint, of which the solid component consists of magnesium fluoride of the particle size 0.1  $\mu\text{m}$  or less and 1 or more silanes selected from  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyltriethoxysilane,  $\gamma$ -glycidoxypropylmethyldimethoxysilane,  $\gamma$ -glycidoxypropylmethyldiethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and  $\beta$ -(3,4-epoxycyclohexyl)ethyltriethoxysilane, and the aforesaid magnesium fluoride is 30 ~ 50 weight % of the solid component and the aforesaid silane, as calibrated by silica, is 70 ~ 50 weight % of the solid component, does not cause blocking, and completed the present invention.

Also, they found that in the case when the aforesaid silane is  $\gamma$ -glycidoxypropyltrimethoxysilane, and 40 ~ 90 weight % of this  $\gamma$ -glycidoxypropyltrimethoxysilane, as calibrated by silica, is replaced by 1 member or more of tetraethoxysilane, tetramethoxysilane, tetraisopropoxysilane, tetra n-butoxysilane, tetra sec-butoxysilane, and tetra t-butoxysilane, hardness of the coat can be increased.

Furthermore, they also found that in the case when the aforesaid silane is  $\gamma$ -glycidoxypropyltrimethoxysilane, and less than 50 weight % of this  $\gamma$ -glycidoxypropyltrimethoxysilane, as calibrated by silica, has been replaced by 1 member or more of methyltrimethoxysilane, methyltriethoxysilane, and methyltriisopropoxysilane, warm water durability of the coat can be increased.

In the following, the present invention is explained in detail.

The solid component of the paint of the present invention is 4.5 ~ 5.5 weight % of the overall compound including the solvent, and 30 ~ 50 weight % of the solid component is magnesium fluoride of the particle size 0.1  $\mu\text{m}$  or less, and 70 ~ 50 weight % of it is at least one member of  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyltriethoxysilane,  $\gamma$ -glycidoxypropylmethyldimethoxysilane,  $\gamma$ -glycidoxypropylmethyldiethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, and  $\beta$ -(3,4-epoxycyclohexyl)ethyltriethoxysilane, as calibrated by silica.

Here, as the ultrafine particles of magnesium fluoride of the particle size 0.1  $\mu\text{m}$  or less, for example, the ultrafine particle magnesium fluoride manufactured by Sumitomo Cement Co. can be used suitably.

Also, as for the binder, a single or a combination of two or more of the aforesaid substances can be used, but the use of  $\gamma$ -glycidoxypropyltrimethoxysilane alone is

particularly preferred. Namely, this is because, in the case when  $\gamma$ -glycidoxypropyltrimethoxysilane is used, various characteristics such as refractive index, adhesion to the substrate material, coat strength, etc. obtained are all higher than in the case when the other  $\gamma$ -glycidoxypropyltriethoxysilane,  $\gamma$ -glycidoxypropylmethyldimethoxysilane,  $\gamma$ -glycidoxypropylmethyldiethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, or  $\beta$ -(3,4-epoxycyclohexyl)ethyltriethoxysilane is used.

Also, as for the compounding amount of these silanes, if they are less than 40 weight % as calibrated by silica (namely,  $\text{RSiO}_{1.5}$ , R : epoxy group-containing organic group), they are less effective as the binder, and if they exceed 90 weight %, the flexibility of the coat which is necessary as the coat for film is degraded, and thus it is not preferable.

Also, among the silanes used in the present invention, for example,  $\gamma$ -glycidoxypropyltrimethoxysilane is extremely good for the flexibility of the coat when used as the binder, but in addition, the coat hardness can be increased by the addition of tetraethoxysilane, tetramethoxysilane, tetraisopropoxysilane, tetra n-butoxysilane, tetra sec-butoxysilane, and/or tetra t-butoxysilane. Here, the compounding amount of tetraethoxysilane, tetramethoxysilane, tetraisopropoxysilane, tetra n-butoxysilane, tetra sec-butoxysilane, and/or tetra t-butoxysilane should be such that the total is 40 ~ 90 weight % (as calibrated by silica) of the unsubstituted residue of  $\gamma$ -glycidoxypropyltrimethoxysilane.

Among these silanes, it is particularly preferable to use tetraethoxysilane rather than the other tetramethoxysilane, tetraisopropoxysilane, tetra n-butoxysilane, tetra sec-butoxysilane, and/or tetra t-butoxysilane, because the compound itself is safe and easy to handle.

Also, as the method to improve the warm water durability (measure of degradation of the coat strength by soaking in warm water) which is one of the evaluation items of the coat characteristics, a good result can be obtained, for example, by adding methyltrimethoxysilane, methyltriethoxysilane, and/or methyltriisopropoxysilane when  $\gamma$ -glycidoxypropyltrimethoxysilane is used. Presumably the reason for this is that the water-repellency is generated in the coat obtained. Incidentally, although the use of methyltrimethoxysilane, methyltriethoxysilane, and/or methyltriisopropoxysilane is superior in attaining adhesion to the substrate material and flexibility, the group of the aforesaid tetraethoxysilane, etc. is superior in the coat strength, and it is preferable to use tetraethoxysilane, etc. together in case the coat strength is required. The compounding amount of methyltrimethoxysilane, methyltriethoxysilane, and/or methyltriisopropoxysilane should be such that the total is less than 50 weight % (as calibrated by silica) of the unsubstituted residue of  $\gamma$ -glycidoxypropyltrimethoxysilane, and the effect can be obtained even with a small amount of addition. Since the adhesion to the substrate material and flexibility of methyltrimethoxysilane, etc. are lower than those of  $\gamma$ -glycidoxypropyltrimethoxysilane, the aforesaid characteristics could be impaired if the substitution ratio exceeds 50 weight %, and thus it is not preferable. Also, methyltrimethoxysilane is the most preferable to methyltriethoxysilane and methyltriisopropoxysilane because of the strength of the coat obtained and the ease of handling.

The solvent used for the paint of the present invention, such as ethanol, methanol, MEK (methyl ethyl ketone), etc., can be adopted by exactly the same selection criteria as the regular paint.

Also, any of spraying method, dipping method, printing method, etc. can be adopted as the coating method, but dipping method, spin-coat method, or gravure-coat method is preferred since the antireflection coat is usually as thin as 0.1  $\mu\text{m}$  level and also required to be uniform in thickness.

The substrate to be coated can be any of PET, polycarbonate, PVC, polyolefin, polystyrene, etc., and by coating the paint of the present invention on any of these, the antireflection coat with antiblocking characteristic can be obtained.

In the case when polymer binder is used, for example, the reaction may not be completed and various active groups may remain on the surface and adhere to cause blocking, but the paint of the present invention does not contain polymer of high viscosity and high boiling point material is not used in it, and thus it can form antireflection coat which does not cause blocking.

[Example]

In the following, the present invention is explained specifically by examples.

(Example 1)

Paint was prepared by the following composition.

MgF <sub>2</sub>	5.0 parts by weight
tetraethoxysilane hydrolyzate liquid	49.1 parts by weight (4.17 parts by weight as calibrated by silica)
$\gamma$ -glycidoxypropyltrimethoxysilane	3.9 parts by weight (4.17 parts by weight as calibrated by silica)
ethanol	142 parts by weight

The paint obtained was coated on 100  $\mu\text{m}$  thick PET film with bar coat, and after drying at 60°C, digested at 120°C, and thus 0.1  $\mu\text{m}$  thick antireflection coat was obtained.

Characteristics of the antireflection coat obtained were studied, and the results are shown in Table 1.

Table 1

Item	Result
Total light transmittance	97.5 %
Permeability	0.4 %
Haze	0.4 %
Wear resistance *1	slight scratches
Blocking test *2	No transfer

\*1 : Back and forth 10 times with #0000 steel wool with 500 g load.

\*2 : Using the sample dried at 60°C for 10 sec, the coated face and uncoated face were contacted with 1 kg load, and after 24 hour at 40°C in 90 % RH, transfer to the uncoated face was examined.

Incidentally, the similar test was carried out on the PET film without the aforesaid coat, and it was found that the total light transmittance was 88.8 %, permeability 0.7 %, haze 0.8 %, and scratches were recognized in the wear resistance test.

(Example 2)

Paint was prepared by the following composition.

MgF<sub>2</sub> : 4.0 parts by weight  
 γ-glycidoxypropyltrimethoxysilane hydrolyzate liquid : 28.3 parts by weight  
 (6.0 parts by weight as calibrated by silica)  
 ethanol : 142 parts by weight  
 n-butanol : 50 parts by weight

Using the paint obtained, 0.1 μm thick antireflection coat was prepared by the same manner as the example 1, and characteristics of the antireflection coat obtained were studied.

The results obtained are shown in Table 2.

Table 2

Item	Result
Total light transmittance	97.5 %
Permeability	0.5 %
Haze	0.5 %
Wear resistance *1	slight scratches
Blocking test *2	No transfer

\*1 : Back and forth 10 times with #0000 steel wool with 500 g load.

\*2 : Using the sample dried at 60°C for 10 sec, the coated face and uncoated face were contacted with 1 kg load, and after 24 hour at 40°C in 90 % RH, transfer to the uncoated face was examined.

(Example 3)

Paint was prepared by the following composition.

MgF<sub>2</sub> : 5.0 parts by weight  
 tetraethoxysilane hydrolyzate liquid : 42.4 parts by weight  
 (3.6 parts by weight as calibrated by silica)  
 γ-glycidoxypropyltrimethoxysilane hydrolyzate liquid : 3.9 parts by weight  
 (1.0 parts by weight as calibrated by silica)  
 methyltrimethoxysilane : 2.7 parts by weight  
 (0.4 parts by weight as calibrated by silica)  
 ethanol : 95.2 parts by weight  
 isopropanol : 50 parts by weight

Using the paint obtained, 0.1 μm thick antireflection coat was prepared by the same manner as the example 1, and characteristics of the antireflection coat obtained were studied.

The results obtained are shown in Table 3.

Table 3

Item	Result
Total light transmittance	97.8 %
Permeability	0.3 %
Haze	0.3 %
Wear resistance *1	almost no scratches
Blocking test *2	No transfer

\*1 : Back and forth 10 times with #0000 steel wool with 500 g load.

\*2 : Using the sample dried at 60°C for 10 sec, the coated face and uncoated face were contacted with 1 kg load, and after 24 hour at 40°C in 90 % RH, transfer to the uncoated face was examined.

[Effect of the invention]

As explained in the foregoing, the paint according to the claim 1 of the present invention can form antireflection coat which does not cause blocking in film without addition of antiblocking agent.

Also, according to the invention of the claims 2 and 3, hardness of the antireflection coat obtained by the paint according to the claim 1 can be raised.

According to the invention of the claims 4 and 5, the warm water durability of the antireflection coat obtained by the paint according to the claim 1 can be improved.

Applicant      Sumitomo Cement Co.